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SEAWATER DESALINATION USING SMART POLYACRYLIC ACID HYDROGEL IN HAQEL-TABUK, KINGDOM OF SAUDI ARABIA (KSA)

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ABSTRACT

In the present study, we prepared polyacrylic acid hydrogel with different concentration (10, 20, 30 mol %) of N, N´- methylene bisacrylamide (BIS) cross-linker, ammonium peroxodisulphate (APS) and N, N, N`, N`- tetramethyl ethylene diamine (TEMD) the reaction proceed by free radical polymerization technique. The chemical structure was evaluated by infrared spectroscopy (FT-IR). The glass transition temperature (T_g) was recorded by differential scanning calorimetery (DSC). The swelling properties of hydrogels were measured in seawater, collected from the beach of Haql city in Tabuk kingdom of Saudi Arabia. The swelling and desalination of water were measured as a factor of time. In future, we are hoping to use the present hydrogel for desalination of seawater in large scale.

KEYWORDS: Seawater Desalination, Smart Polyacrylic Acid, Hydrogel & Haqel-Tabuk

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Original Article

1. INTRODUCTION

Hydrogels are often referred to as “super absorbers” due to their huge uptake of water or aqueous solutions [1]. It is not uncommon for the solvent capacity of hydrogels to exceed several 100 times their own weight. It is this feature, in particular, which has generated so much scientific interest across a wide range of fields for this class of materials. The structures of hydrogels are cross-linked polymeric chains, which usually carry charges attached to their backbones [2]. The affinity to water has offered hydrogels on one side a range of large volume applications and on the other; they are also used for specialised high-tech products. In to the former category fall typically, personal hygiene products. They are used for the fast absorption of high quantities of bodily fluids [3]. Other examples in the same category are the use as underwater-cable insulations, the addition to agricultural soil to retain water close to the plants or as a separating agent for water-oil slurries e. g. in down the hole applications [4,5]. Into the category of specialised applications fall high-tech applications, that needs only minor amounts of the material, but high level of sophistication in its design. On the forefront of this field are the stimuli responsive gels that switch their swelling state due to an external stimulus such as salt [6], temperature [7], light [8], pH [9], electrical current [10], or the presence of certain small molecules [11]. Among the numerous practical applications of stimuli responsive, hydrogels are the controlled release of drugs [11, 12], the use as actuators in fluidics [13].

Seawater desalination is in the focus of interest today, due to a shortage of fresh water resources in many parts of the world [14]. A number of drivers are currently straining the natural freshwater resources, such as

population growth, increasing standard of living, climate change, and depletion of the fossil aquifers [15, 16].

One of the possible solutions is producing fresh water from the oceans by the removal of the contained salt (about 3.5 wt. %). Seawater contains a large number of different ions, but mostly sodium chloride (87 wt. %) of the ionic content) and a number of divalent ions [17]. Seawater desalination is already undertaken on a large scale by a number of countries such as Saudi Arabia, the United Arab Emirates, the USA, and Spain [14]. The global installed capacity is expected to reach 62-106 m^3 of freshwater production per day by 2015 [18]. All methods which separate salt from water require energy to overcome the osmotic pressure seawater (about 27 bar). Several technologies are in use for the production of freshwater, the highest market shares are held by reverse osmosis and a number of distillation processes [19-20].

Haql is a city in the northwest of Saudi Arabia, near the head of the Gulf of Aqaba, adjacent to Aqaba across the Jordanian border. The coasts of Egypt, Israel and Jordan can be seen from Haql.

In the present study, we focused on preparation of polyacrylic acid hydrogel with different concentration of cross-linker. The influence of cross-linker concentration on the volume degree of swelling has been discussed. Samples of water from Haql beach have been collected to study the desalination through swelling of hydrogel. The time was taken as factor in the swelling parameters. The final results were observed in lowering salt concentration of seawater.

2. EXPERIMENTAL

2.1. Material

Acrylic acid (AA) (99% Merck, Germany), *N, N, N', N'*-tetra methyl ethylene diamine (TEMED) (99%, Acros, Germany), methylene bisacrylamide MBA (99%, Aldrich, Germany), ammonium per sulfate (APS) (99% Merck, Germany). Other chemicals were used as received.

2.2. Instruments

Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer spectrophotometer at room temperature. The samples were milled with dry potassium bromide KBr (Merck 99%) and pressed to pellets. Perkin Elmer Differential Scanning Calorimeter (DSC) Pyris 1 was used for the determination of T_g of solid polymers. The thermogram was recorded at heating and cooling rate of 5 °C/min. The morphology of the polymer were examined by Scanning Electron Microscopy (SEM) using a Zeiss NEON 40 instrument (USA); 2 kV (30 µm aperture). Sputter coater is a Bal-Tec SCD 500 with a film thickness monitor QSG 100. We applied approx. 4 nm of gold-palladium (Au: Pd = 80:20). Salinity/SG Refractometer 0 - 100ppt / 1-1.070SG ATC for measuring the salt concentration of water, the RSA0100A displays readings in parts per thousand (ppt) or specific gravity, while the RSA0028A display readings in % of salt.

2.3. Synthesis of Polyacrylic Acid Hydrogel

The PAA hydrogel were prepared according to the following procedure;

In test tube, 0.05 molAA and 0.001 mol BIS (cross-linker, 2 mol% over the total monomer concentration) were dissolved in 10 mL deionized water, under stirring in water bath at 60 ^oC. After deoxygenation of the solution by N2 bubbling for 30 min, 0.1 g APS (dissolved in 2 mL deionized water) and 3 drops of TEMED were added. The formation of the gel was almost immediate. The gel was cold in refrigerator for two hours, then removed from test tube and cutting small pieces 1 cm in thickness. Gel was dried overnight in oven under reduced pressure.

IR (KBr): ν (cm^{-1}): 2990 (s) (CH_2, CH), 1720 (s) (C=O, carboxyl), 1610 (s) (C=O, amide).

2.4. Hydrogel Swelling

Dynamic swelling experiments were performed by placing the discs in seawater at 30 ^{o}C 0.1°C (in a thermostated bath) and measuring their weight gain as a function of time. The discs were re-moved from the water, dried quickly and carefully with filter paper and weighted.

The degree of swelling at different times can be calculated from the following equation:

$$W(\%) = m\text{-}mo\ /m \times 100 \quad (1)$$

Where, m_o and m are the weights of the initial dry sample (xerogel) and of the hydrogel, respectively.

2.5. Seawater Desalination

The process envisioned for seawater desalination with hydrogels follows three steps. First, the dry hydrogel was immersed in 50 ml seawater. The swelling was determined as a function in time for each 1 h. For each swelling measurement, the salinity of water was measured by refractometer. The polymer is subjected to an external stimulus, in this case hydrostatic pressure, to free the solution from it (step 3). The water received in the end has a lower salt concentration than initially used, thus constituting a successful desalination

3. RESULTS AND DISCUSSIONS

Free radical polymerization was used to prepare polyacrylic acid hydrogel. Three different molar concentration of cross-linker MBA (10, 20, and 30) was used to produce three different hydrogel. The effect of cross-linker concentration has been sharply observed. **Table 1** cleared the amount of cross-linker, APS, TEMED.

Table 1: The Amounts used for Preparation of Polyacrylic Acid Hydrogel and the Glass Transition Temperature

Hydrogel	AA g/mol.	MBA g/mol	APS (g)	TEMED (g)	T_g (^{o}C)
A-10	3/0.042	0.642/0.0042	0.2	0.02	100
B-20	3/0.042	1.295/0.0084	0.4	0.04	130
C-30	3/0.042	1.943/0.0126	0.6	0.06	140

AA acrylic acid; MBA methylene bisacrylamid; APS ammonium persulphate; TEMED*N, N, N', N*'-tetra methyl ethylene diamine; T_g glass transition temperature.

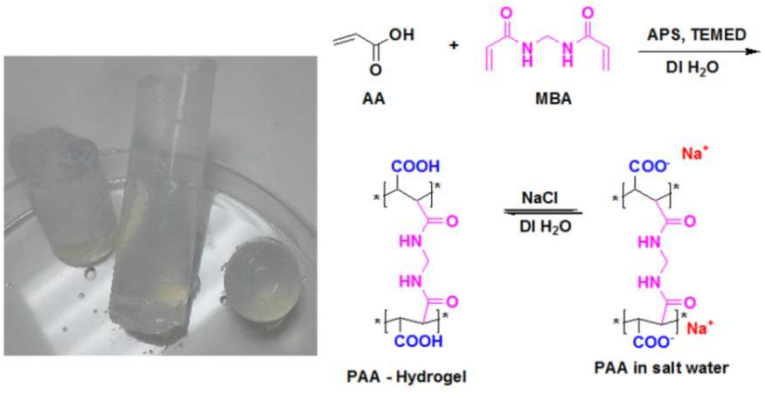

Figure 1: Preparation of Polyacrylic Acid Hydrogel

3.1. FT-IR Spectral Analysis

KBr FT IR spectra showed characteristic bands, we can observe an important sharp band at 1720 cm^{-1} **Figure. 2**. This band is assigned to the vibrations of the carbonyl group of the carboxylic group. Kim et al. observed this band at 1709 cm^{-1} and correlated it with the intermolecular hydrogen bonds among the carbonyl groups of the polymer [14]. At 1610 cm^{-1} stretched band for CONH of cross-linker. CH and CH_2 polymer chain has appeared at 2990 cm^{-1}. **Figure** proved that, all data was in logic with the chemical structure.

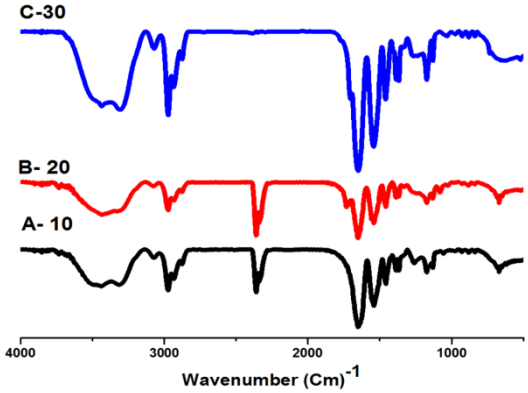

Figure 2: FTIR Spectra KBr for Hydrogels

3.2. Thermal Analysis

3.2.1 Thermal Gravimetric Analysis

Figure 3 Showed the thermal stability of hydrogels, which was recorded by thermal gravimetric analysis. Hydrogel A-10 showed one step decompression, while hydrogel B-20 and C-30 showed decomposition in two steps, which can interpret to increasing in cross-liker composition.

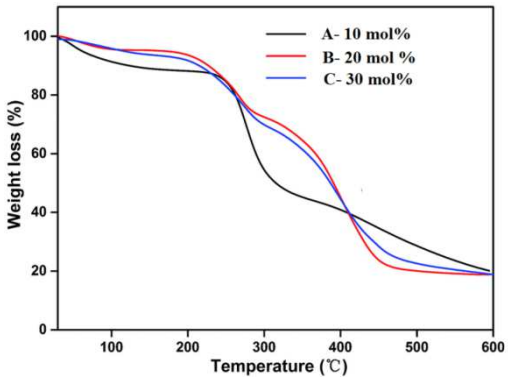

Figure 3: TGA of Xerogel Samples

3.2.2. Differntional Scanning Calomerimetry

The glass transition temperature (T_g) has been recorded by Differential Scanning Calorimeter of dried samples at heating rate 5 ^oC/min, as described above in the experimental part. The $T_g$value was taken as the midpoint inflection. The (T_g' *s)* values have been tabulated in **Table 1** for hydrogel A-10, B-20 and C-30. **Figure 4** showed a single T_g for each sample, which indicates the formation of random polymerization [1]. Hydrogel A-10showed T_g at 100^{o}C which is the lowest value. By increasing the concentration of cross-liker, the T_gs were increased 130 ^{o}C and 140 ^{o}C for B-20 and C-30, respectively. This is due to the increasing cross-linking density, which further increased crystallinity of hydrogel.

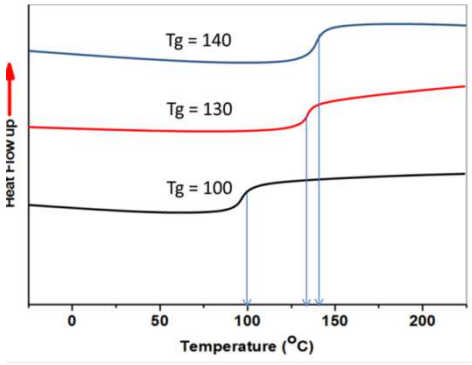

Figure 4: DSC shows the T_g of Hydrogel

3.3. X-Ray Diffraction

The X-ray diffractograms (Figure 5) showed a broad peak at 2Θ = 20°. This peak is associated to the intra-chain segments distance of 0.45 nm (determined using the Bragg´s law). **Figure 5** showed increasing in crystallinity of hydrogel C-30, B-20 and A-10 respectively, due to increasing the cross-linker density, which effect on the gel pore size and increase the intermolecular interaction.

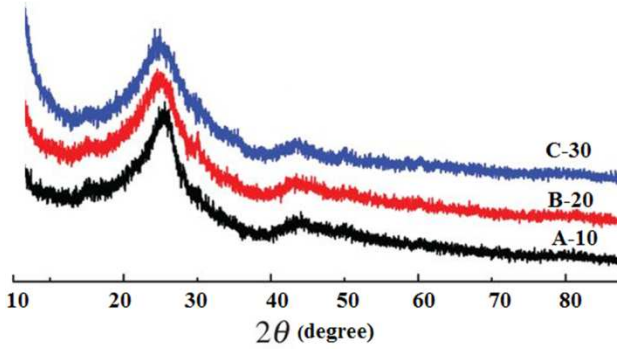

Figure 5: X-Ray Diffraction of Xerogel (dry gel)

Swelling and Collapsed Properties

Swelling is a typical process of polymeric networks and one of the most important features used in applications. By swelling, the network structure is extended as a suitable solvent is taken up into it, and the previously liquid phase is solidified and immobilised. Swelling isused extensively for the characterisation of gels as the equilibrium swelling.

The degree of swelling of a network is quantified by the ratio of solvent to polymeric material. In the swollen gel, this ratio can either be volume or mass as described in equation (1).

When placing dry polymer in contact with a solvent reservoir, it will take up solvent and swell. This is a time dependent process, and therefore the swelling degree is time dependent. When dry polymer is in contact with a solution, in the beginning m_o holds as no solvent is present in the polymer and m increases upon solvent. **Table 2** clears the degree of swelling and desalination ratios of hydrogel with different mole ration of cross-linker. **Figure 6** describes the relation of degree of swelling as a time function, and demonstrated the highly swelling value with the lowest concentration of cross-linker, which might be attributed to the largest pore size in A-10 than B-20 and C-30 which allow absorbing much more water interior. From Table 2 and Figure 7, we observed the highest desalination occurred for A-10, with the largest pore size that might be due to lower density of cross-linker with intensively carboxy late ions charges for absorption of

much more amount of salt.

Table 2: The Change of Volume Degree of Swelling and Salinity with Time

Time/h	Degree of swelling %			Salinity (ppt)		
	A-10	B-20	C-30	A-10	B-20	C-30
1	40	30	10	58	62	62
3	150	130	80	50	56	58
6	200	180	120	43	50	53
12	260	240	140	21	25	28
15	290	255	155	8.2	10.5	18
18	300	257	157	5.4	7.6	13
24	304	260	157	3.2	5.3	10.2

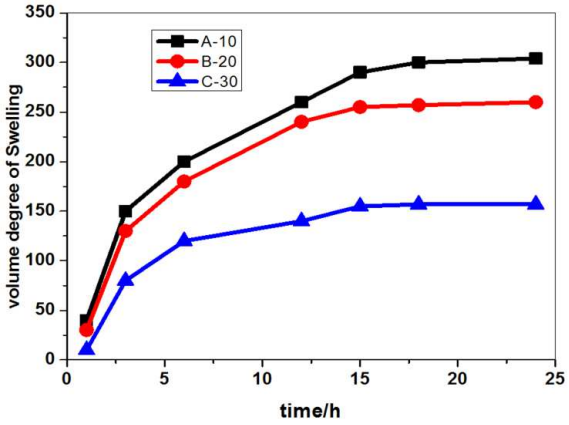

Figure 6: The Volume Degree of Swelling with Time in Hours

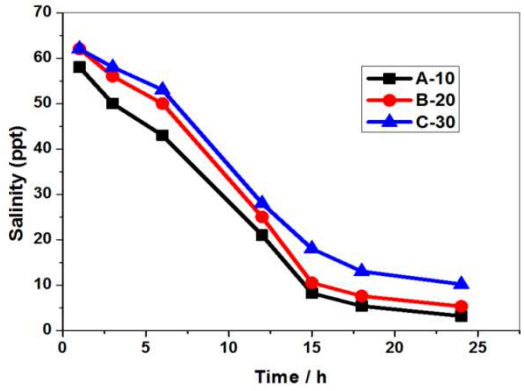

Figure 7: The Salinity (ppt) with Time in Hours

3.5. Morphological Feature (SEM)

Figure 8 is the Scanning Electron Microscopy (SEM) image obtained at a magnification of 1000× hydrogel A-10, B-20 and C-30. The porosity of hydrogelA-10 surface increases the whole surface, looks like waxy with cross-linking. As increasing the concentration of cross-linker from B-20 to C-30 respectively, we noticed decreased in pore size.

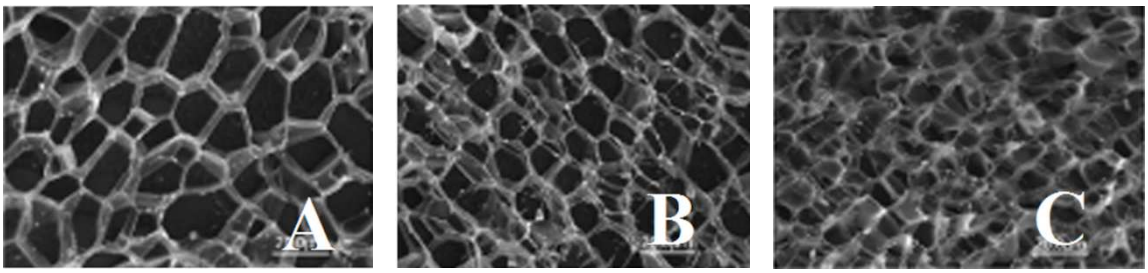

Figure 8: A-C SEM of Hydrogels at 1000x Magnification

4. CONCLUSIONS

Here, we synthesized new functional polyacrylic acid hydrogel with different mole ratio of cross-linker to study the effect of cross-linker in the degree of swelling and desalination of seawater. The new region in HaqlTabuk KSA was selected for this study, due to the highly salinity of water. All polymers gel were evaluated by chemical methods and physical methods and showed logic results with their structure. The relation of degree of swelling as a time function demonstrated the highly swelling value with the lowest concentration of cross-linker, which might be attributed to the largest pore size in A-10 than B-20 and C-30 that allow absorbing much more water interior. We also observed the highest desalination occurred for A-10, with the largest pore size that might be due to lower density of cross-linker with intensively carboxy late ions charges for absorption of much more amount of salt.

5. ACKNOWLEDGMENT

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6. CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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Graphical Abstract

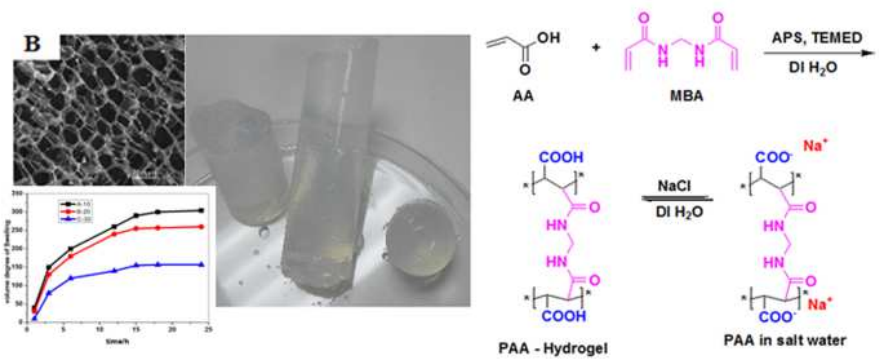

Figure 9